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Copolymerization of Pyrrole and Thienyl End Capped Cyclohexanone Formaldehyde Resin with Ce(IV) Oxidic Dibenzoate

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Abstract

Block copolymers of polypyrrole (PPy) and thienyl end capped cyclohexanone formaldehyde resin (ThCFR) were synthesized via chemical oxidative polymerization of (Py) and ThCFR in the presence of cerium (IV) oxidic dibenzoate (CODB). The treatment of Py with CODB was maintained in non-aqueous media at room temperature. Several solvents including toluene, dichloromethane (DCM), were used. Besides the role of reaction media, the effect of ceric (IV) oxidic compound on polymerization was investigated. Reactions with constant amount of Py, and CODB to Py mol ratios of 0.33:1.0, 0.5:1.0 and 1.0:1.0 were observed. The results showed that in one-hour limited time, block copolymers could be obtained in toluene and dichloromethane with CODB: Py: ThCFR mol ratio of 1.0: 1.0: 0.01. Conductivities of polypyrroles were determined by 4-point probe technique. Block copolymers were prepared in dichloromethane and toluene, respectively.

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Keywords: Cerium, conductivity, oxidative polymerization, polypyrrole, ketonic resin

1. Introduction

Conductive (or electro-active) polymers are a special type of polymer with extensive π-electron delocalization along their backbones that give rise to interesting optical properties and allows them to become good electrical conductors (typically when oxidized or reduced) (De Leon & Advincula, 2015; Chiang et al., 1977). Polypyrrole is an example of heterocyclic conductive polymers (Dall'Olio et al., 1968; De Leon & Advincula, 2015).

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Conductive polypyrrole has received considerable attention because it can be prepared both electrochemically (Diaz et al., 1979; Kızılcan et al., 2001) and by chemical oxidation and because it has relatively good stability in the conducting oxidized form. However, PPy is a hard, brittle, and nonprocessable solid that is insoluble in common solvents (Kızılcan et al., 2001; Gardini, 1973; Sarac et al., 1994).

Still polypyrrole is one of the most investigated conducting polymers, owing to its facile synthesis, good conductivity, redox properties, long-term environmental stability and biocompatibility as polymer in vivo (Hafaid et al., 2010), and has shown promising applications including sensors (Chartuprayoon et al.,2010), actuators (Cho et al., 2008), photovoltaic/solar cells (Guo et al., 2010; Wu et al., 2008), electromagnetic interference shielding (Joo & Lee, 2000), and corrosion protection (Schaftinghen et all., 2007). In addition, PPy nanocomposites have been shown biodegradability and biocompatibility, which are potentially useful in drug delivery and tissue engineering (Guimard et al., 2007; Ge et al., 2007; Liao et al., 2012).

Polymerizations initiated by a reaction between an oxidizing and a reducing agent are called redox polymerizations. Redox polymerization has found wide applications in initiating polymerization reactions and has been specifically of industrial importance. The essence of redox initiation is a reduction-oxidation process. In this process an oxidant, i.e., Ce(IV) or Mn(III) forms initially a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization (Özturk & Cakmak, 2007). There are many reports in the literature on the block copolymer synthesis. Initiation by a redox process is only a method to obtain these types of polymers (Özturk & Cakmak, 2007; Nagarajan & Srinivason, 1994; Nagarajan & Srinivasan, 1995; Wodka, 1993; Nagarajan et al., 1994). The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions are minimized (Özturk & Cakmak, 2007; Cakmak, 1993).

Ceric ions in acidic media are well-known oxidizing agents for various organic substrates (Özturk & Cakmak, 2007; Trahanovsky et al., 1967). Also, these ions, either by themselves or in combination with reducing agents function as initiators for polymerization (Özturk & Cakmak, 2007; Leza & Guzman, 1999; Saldick, 1956; Venkatakrishnan & Santappa, 1958; Ananthanarayanan & Santappa, 1965; Mino & Kaizerman, 1958; Misra & Arya, 1984; Fernandezn & Guzman, 1989; Sudhakar et al., 1979). A first attempt to initiate polymerization by Ce(IV) in organic solvents was performed in 1979 by Singh et al. (Özturk & Cakmak, 2007; Singh et al., 1979) who observed that the solvent (toluene) inhibits the redox initiating process for the polymerization of acrylonitrile. The suitable reducing agents reported in the literature are alcohols (Özturk & Cakmak, 2007; Mino et al., 1959), polyoils (Özturk & Cakmak, 2007; Mohanty et al., 1979), ketones (Özturk & Cakmak, 2007; Subramanian & Santappa, 1968), acids (Özturk & Cakmak, 2007; Subramanian & Santappa, M, 1968, amines (Özturk & Cakmak, 2007; Saha & Chaudhuri, 1972), thiols (Özturk & Cakmak, 2007; Chakrabarty & Chaudhuri, 1985), and thiourea (Özturk & Cakmak, 2007; Pramanick et al., 1979).

Most of the commercial resins are generally solid materials with low molecular weight. Also they can be processed easily. These types of resins are mainly used in surface coatings, varnishes, inks, and textile and paper industries as additive materials. Cyclohexanone formaldehyde resin (CFR) is a low molecular weight and shows unique compatibility with a great number of polymers (Kızılcan & Akar, 1996). It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. Due to its good compatibility, it is usually used as a coating additive. Copolymers of ketonic resins have been the subject of recent research since the ketonic resin segments improve adhesion, solubility, gloss and light stability of parent polymers. These copolymers have been synthesized via condensation polymerization (Uyanık et al., 1991; Uyanık et al., 1998; Uyanık et al., 2001; Kızılcan & Koşar, 2012), free radical polymerization (Kızılcan, 1999), redox polymerization (Ustamehmetoğlu et al., 2004; Ustamehmetoğlu et al., 2011; Ustamehmetoğlu et al., 2012; Kızılcan & Ustamehmetoğlu, 2005; Kızılcan et al., 2011), promoted cationic polymerisation routes (Ergun et al.,2007) and atom transfer radical polymerization (Çanak et all., 2011 and 2012). The block copolymers of N-vinyl carbazole and α,ω-dihydroxy polydimethylsiloxane have been produced in one step at room temperature with the redox initiation system of ceric salt and hydroxyl group of PDMS (Akar et al., 2007).

In this work, block copolymers of polypyrrole (PPy) and thienyl end capped cyclohexanone formaldehyde resin (Th-CFR) were synthesized via chemical oxidative polymerization of (Py) and ThCFR in the presence of cerium (IV) oxidic dibenzoate (CODB). The treatment of Py with CODB was maintained in non-aqueous media at room temperature. Several solvents including toluene, dichloromethane, were used. Besides the role of reaction media, the effect of ceric (IV) oxidic compound on polymerization was investigated.

2. Experimental

Materials

Pyrrole (Sigma-Aldrich), cerium (IV) ammonium nitrate (Alfa Aesar), benzoic acid (Merck), sodium hydroxide (Sigma-Aldrich), dichloromethane (Merck), toluene (J.T. Baker) and acetone were all reagent-grade chemicals of highest purity and were used without further purification. All solutions were prepared freshly before each experiment.

Analyses

Infrared (IR) spectra were recorded on a Jasco FTIR 5300 Fourier transform infrared spectrometer.

Electrical conductivities of polymers were determined by four point probe technique using Keithley 2400 model multimeter, Lucas Labs 302 model probe holder and SP4-180-TFS type probe. Thin pellets with typical sample diameter of 13 mm were prepared by compaction of the polymer powders under 10 tons of pressure.

$$\sigma = V^{-1} \cdot I \cdot (\ln 2/\pi d_n) \quad (1)$$

where V is the potential (Volt), I is current (Amper) and d_n is the thickness of the samples (cm).

The morphology of the products was examined by scanning electron microscopy (SEM; ESEM XL30 ESEM-FEG, Philips) and the samples for the SEM measurement were prepared by platinum coating.

Synthesis of thiophene-2-carbonyl chloride and cyclohexanone formaldehyde resin

Synthesis of CFR - Into a three-necked flask equipped with a stirrer and a condenser, 104 ml of cyclohexanone, 25 ml of cyclohexane and 30 ml of 37 per cent formalin were added. When the temperature of the mixture was raised to 65-70 °C, refluxing started. Subsequently, 100 ml of 37 per cent formalin and 3.64 ml of 20 per cent NaOH were mixed and added continuously at gradually increasing rate sufficient enough to maintain vigorous refluxing. The reaction was further continued under pH values of 11-12 for 3 hours with 20 per cent NaOH aqueous solution. After reaction time was completed, two layers were formed. The cyclohexanone formaldehyde resin was separated and purified by decanting the water layer. CFR was washed several times with hot water until it was free from formaldehyde odour, and it was dried at 110 °C in vacuum for 5 hours (Kızılcan and Akar, 1996).

Synthesis of the comonomer ThCFR - In a flange flask fitted with a multiple socket cooled carrying a mechanical stirrer, a dropping funnel and a thermometer, 35 ml of chloroform, 10 g of CFR and 2 ml pyridine were placed. The flask was cooled on an ice bath, while stirring vigorously under nitrogen. Subsequently, the solution of 2.67 ml of ThCCl in 5 ml of chloroform was added to the resin solution dropwise under stirring. The pink-coloured solution was allowed to stand at 0 °C for 24 hours, then was diluted with 150 ml of chloroform and transferred to a separatory funnel. It was washed successively with several portions of diluted aqueous HCl (5 per cent of 100 ml) water-saturated aqueous sodium hydrogen carbonate and hot water. Eventually, the mixture was poured into 50 ml of hexane. Then the precipitate was dried at 25 °C in vacuum. The resin was modified with thiophene-2-carbonyl chloride using mol ratio of CFR to ThCCl as 1/2 to give ThCFR (Ates et al., 2015).

Sythesis of Ce(IV) Oxidic Dibenzoate

Benzoic acid (9.76 g, 0.08 mol) was placed in a reaction vessel and pure water (80 ml) was added. Sodium hydroxide (3.2 g, 0.08 mol) was added slowly through a dropping funnel at room temperature. The mixture was stirred for 15 minutes, so a 0.57M sodium benzoate solution was produced. Ceric ammonium nitrate (10.96 g, 0.02 mol, 0.25 M) was dissolved in water (80 ml) and the solution was added to the sodium benzoate solution through a dropping funnel over a period of 15 minutes. A light yellowish thick material precipitated. The solution was filtered and washed with water, and finally dried at 45 °C for 24 hours (Hawkins & Mauermann, 1995).

Preparation of Pyrrole - Thienyl End Capped Cyclohexanone Formaldehyde Resin Copolymers

Resin was dissolved in solvent (10 ml). After stirring for 15 minutes, constant amount of pyrrole (0.3 ml) was added and the stirring process was continued. Oxidation solution was prepared with same solvent (40 ml) as used for polymer-solution. Synthesized cerium (IV) oxidic dibenzoate was added with different ratios to solvent and after 15 minutes of stirring compounded drop wise with polymer-solution. While mixing solutions a black powder formed almost instantaneously. The color of the solution changed within few minutes from first pale greenish to finally black. Experimental work was carried out at room temperature and stirring process was maintained with a magnetic stirrer. After polymerization, the powder was filtered by means of filter paper and funnel, washed with solvent and acetone several times, and dried at 45 °C.

3. Results and Discussion

In this study, copolymers of polypyrrole and thienyl end capped cyclohexanone formaldehyde resin (ThCFR-b-PPy) were synthesized with a novel cerium (IV) based oxidant (CODB). Copolymerization reaction is demonstrated in Figure 1.

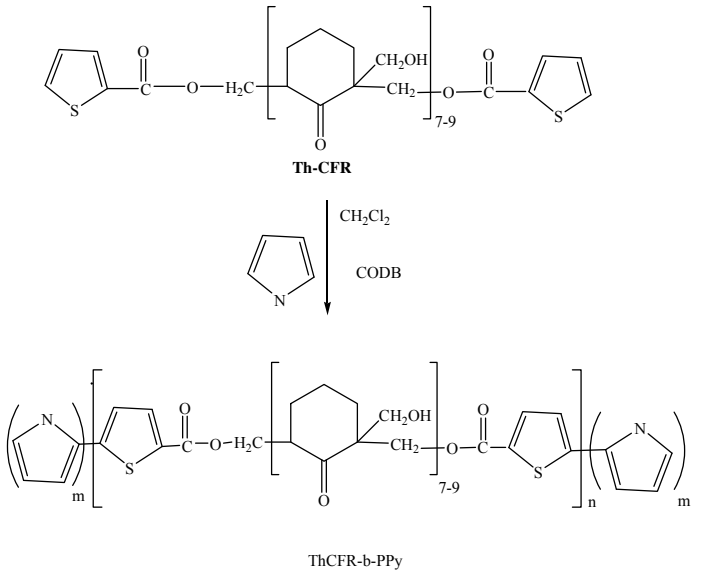

Fig. 1. Synthesis of ThCFR-b-PPy.

Reaction conditions were summarized in Table 1. The influence of solvent type, CODB to Py mol ratio and reaction time on the yield and conductivities of the copolymers were investigated. As the results were compared in terms of yield of the copolymer it was found that increasing the mol ratio of CODB to Py or reaction time increased

the yield of product. The effect of the solvent type was found to be negligible. Conductivities of copolymers were measured in the range of 10^{-7}-10^{-6} S/cm. It was suggested that the long treatment of pyrrole with the oxidant resulted in copolymers with low electrical conductivities.

Table 1. Summary of the experimental work.

#	Solvent	Resin	n_{CODB}/n_{Py}	n_{py}/n_{resin}	Time (h)	Yield (%)
1	Dichloromethane	-	0.5	-	24	26
2	Dichloromethane	ThCFR	0.5	100	1	3
3	Toluene	ThCFR	0.5	100	1	2
4	Dichloromethane	ThCFR	0.5	100	2	3
5	Dichloromethane	ThCFR	0.5	100	24	26
6	Dichloromethane	ThCFR	1.0	100	24	53
7	Dichloromethane	ThCFR	0.5	50	24	22
8	Dichloromethane	ThCFR	0.33	100	24	9
9	Dichloromethane	CFR	0.5	100	24	22

The structures of comonomer ThCFR and copolymer ThCFR-b-PPy were confirmed by spectroscopic investigations. Infrared spectrum of the modified resin is outlined in Figure 2. Absorption bands at 3450 cm^{-1} including stretching vibrations of –OH groups. The FTIR spectrum of ThCFR indicated signal corresponding to aromatic groups of the thiophene and gave the characteristic ester band at 1712 cm^{-1}. Aromatic ring vibration of thiophene –C=C– appears as a peak at about 3050 cm^{-1}, 1600 cm^{-1} and out of plane stretching vibrations of =C–H has a peak at 750 cm^{-1}. Figure 3 represents the spectrum of ThCFR-b-PPy. The strong absorption bands at 1400 and 1500 cm^{-1} belong to pyrrole ring and support formation of the copolymer.

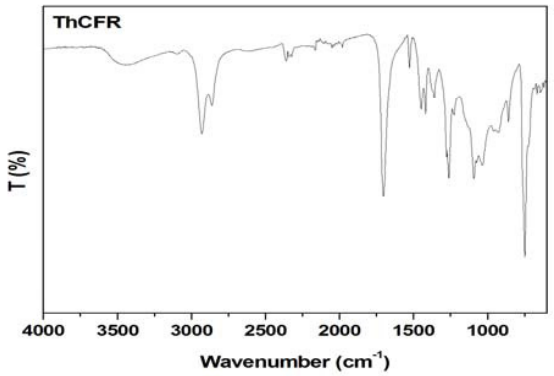

Fig. 2. FTIR spectrum of the comonomer, ThCFR.

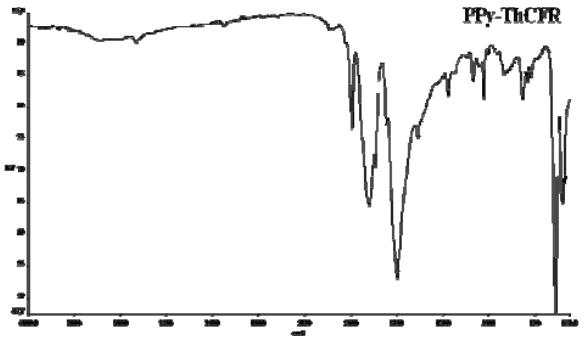

Fig. 3. FTIR spectra of the copolymer, ThCFR-b-PPy.

The surface properties of ThCFR-b-PPy copolymer (Sample #7) is demonstrated in Figure 4. Morphology of the copolymer consists of smooth blocks and spherical particles that are attributed to resin and polypyrrole, respectively.

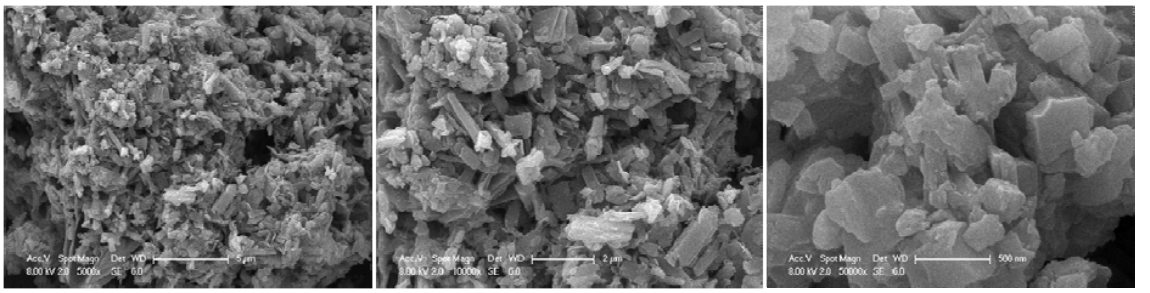

Fig. 4. SEM micrographs of ThCFR-b-PPy, copolymer.

This study has brought a new approach to synthesis of copolymers of polypyrrole suggesting the use of a novel Ce (IV) based oxidant. The organic origin of the oxidant enables performing the copolymerization reactions in solvents such as dichloromethane and toluene, the solvents favorable for solubility of various insulating polymers.

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